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(71) Applicant: SHELL OIL COMPANY [US/US]; One Shell Plaza, P.O. Box 2463, Houston, TX 77252 (US).

(72) Inventor: JOB, Robert, C. ; 12126 Westmere, Houston, TX 77077 (US).

(74) Agents: BIELINSKI, Peter, A.; Shell Oil Company, One Shell Plaza, Houston, TX 77252 (US) et al.

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(54) Title: POLYMERIZATION PROCESS AND CATALYST

(57) Abstract

A process and a catalyst for the production of elastomeric, primarily stereoregular poly-α-olefin characterized by a relatively narrow distribution of relatively short block lengths, which comprise the polymerization of α-olefin of at least 3 carbon atoms in the presence of a catalyst which comprises the reaction product of a magnesium oxy compound and a tetravalent titanium halide in the presence of an electron donor, an organoaluminum compound and a selectivity control agent which is an aromatic heterocyclic nitrogen compound.

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POLYMERIZATION PROCESS AND CATALYST

Field of the Invention

This invention relates to the production of
elastomeric, primarily stereoregular
5   polyolefins, to a process of producing such
polymers and to a catalyst useful in such a
process.

Background of the Invention

Several U.S. patents, to Natta, e.g., U.S.
10   3,112,300 and U.S. 3,112,301, describe steric
structural types for polypropylene and other
poly-α-olefins wherein the α-olefin has 3 or
more carbon atoms. Using polypropylene as an
example, a polypropylene is termed "isotactic"
15   if the methyl groups are all aligned on the same
side of the straight polymer chain. If the
methyl groups alternate from one side of the
chain to the other, the polymer is termed
"syndiotactic." These two forms containing a
20   regular steric arrangement of methyl groups,
taken together, are generically termed
"stereoregular." In contrast, a polypropylene
in which the methyl groups are randomly arranged
on both sides of the polymer chain is termed
25   "atactic" or "stereo-irregular."

The two more conventionally encountered
physical forms of polyolefin polymers such as
polypropylene are crystalline and amorphous,
which terms refer to the crystalline character,
30   or lack thereof, of the polymer. It is known,
for example, that crystalline polypropylene is
of either the isotactic or syndiotactic
structure and amorphous polypropylene is
generally of the atactic structure. Polyolefins

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such as polypropylene which have elastomeric
properties are somewhat different. U.S. Patent
4,3353,225 discloses a fractionable elastomeric
polypropylene which is said to have an isotactic

5   content of 55% or less and also contain some
syndiotactic and also some atactic structure.
This patent and other patents directed to the
catalyst used to produce the elastomeric polymer
contain considerable information on the nature

10   of the elastic-type polyolefins. A number of
earlier U.S. patents, e.g., U.S. 3,175,999, U.S.
3,257,370 and U.S. 3,258,455, had disclosed
polypropylene having elastomeric properties.
Another earlier U.S. patent, U.S. 3,278,512, had

15   disclosed primarily isotactic polypropylene
polymers having elastomeric properties.
Syndiotactic polypropylene historically has
involved a somewhat different method of
production but such is known from U.S. 3,335,121

20   and U.S. 3,364,190, for example. A catalyst
composition useful for the production of high
molecular weight rubbery material from propylene
is disclosed in U.S. 3,329,741.

        Almost all of the polypropylene which is
25   used commercially is crystalline isotactic
polypropylene. Of lesser commercial importance
is atactic polypropylene, in part because of its
lack of strength. It would be of advantage to
provide an improved process for the production

30   of polyolefin polymers, wherein the olefin is an
α-olefin of at least 3 carbon atoms, which are
elastomeric and primarily stereoregular.

Summary of the Invention
        The present invention provides a process

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for the production of elastomeric, primarily
stereoregular polymers of α-olefin of at least 3
carbon atoms and to the catalysts useful in the
process. More particularly, the invention

5   provides a process for the production of such
polymers which employs a catalyst formed from
(1) a catalyst component derived from reaction
of a magnesium oxy compound and a tetravelent
titanium halide in the presence of an electron

10   donor, (2) an organoaluminum compound and (3) a
selectivity control agent of specified type. In
the process of the present invention, the choice
of selectivity control agent will largely
determine the degree of elastomeric character

15   and the nature of the stereoregularity exhibited
by the elastomeric, primarily stereoregular
polyolefin. The selectivity control agents
useful in the present invention are aromatic,
heterocyclic nitrogen compounds.

20   Description of the Invention
       The polyolefin polymers of the invention
are polymers of α-olefins of at least 3 carbon
atoms. The preferred class of α-olefins
comprises propylene and butylene and

25   particularly preferred is propylene. Largely
for convenience, the invention will be
illustrated in terms of propylene and
polypropylene polymers although it should be
understood that the invention is also applied to

30   polymers of other α-olefins of at least 3 carbon
atoms. The "normal" well-known polypropylenes
are generally high molecular weight materials
which consist of blocks of monomer units of
relatively or extremely long average block

35   length (L) and which are isotactic (<L iso>),

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for example having 50 to 200 monomer units. the
prior art isotactic polymers which are prepared
with a supported magnesium halide catalyst are
of short isotactic block length, e.g., from
5   about 6 to about 15 monomeric units, but
normally contain a wide distribution of polymer
blocks of varying length. These prior art
polymers are characterized by having relatively
low tensile strength and by being tacky to the
10   touch.

The polyolefins of the present invention
are characterized by having a narrow
distribution of relatively short block lengths,
by having relatively high tensile strength and
15   by being non-tacky to the touch. By "block
lengths" is meant the number of recurring
monomer units, for example, propylene units,
which on the average occur before there is a
defect in the polymer chain. By "defect" is
20   meant that the symmetry of the recurring units
is ended and there are units of a different
structure. By way of specific illustration, a
block length of isotactic units is ended by the
presence of a syndiotactic unit or units in the
25   polymeric chain. It is thought likely that the
average block length, as determined by a
numerical integration of the pentads which occur
in the ^{13}C-NMR spectrum, has a great effect on
the properties of the polymer. For example, a
30   relatively short block length of from about 7 to
about 15 monomer units tends to be found in a
flexible or rubbery polymer which exhibits good
elastomeric properties and is relatively strong
with a tensile strength of from about 1500 psi
35   to about 3000 psi. Alternatively, block lengths

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of greater than about 50 are characteristic of
very stiff, highly crystalline isotactic
polypropylene of the commercial type.

5   the process disclosed by the above U.S.
4,335,225 produces an elastomeric polypropylene
having up to 55% and preferably less of
isotactic polypropylene. The process requires a
zirconium or hafnium catalyst supported on
partially hydrated alumina. These catalysts

10   exhibit extremely low productivities, on the
order of 1% to 2% of the productivity of the
catalysts of the present process, and are not
used commercially to any appreciable extent.

          the polyolefins of the present invention

15   are produced in the presence of a catalyst
derived from a procatalyst of a type which is
well known. This procatalyst is the reaction
product of a magnesium oxy compound of the
formula MgR_1R_2, wherein R_1 is alkoxy or aryloxy

20   and R_2 is alkyl, aryl, alkoxy, aryloxy or
halogen, preferably alkoxy, aryloxy or halogen,
and a tetravalent titanium halide, which
reaction takes place in the presence of an
electron donor and, preferably, a halogenated

25   hydrocarbon. Such procatalysts, also termed
solid catalyst components, are conventional and
commercial. The olefin polymerization catalyst
is formed from this procatalyst, an
organoaluminum compound and an aromatic

30   heterocyclic nitrogen compound as selectivity
control agent.

          Examples of magnesium oxy compounds useful
as precursors of the procatalyst are alkoxy or
aryloxy magnesium halides such as

35   isobutoxymagnesium chloride, ethoxymagnesium

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bromide, phenoxymagnesium iodide,
cumyloxymagnesium bromide, naphthoxymagnesium
chloride and $Mg_4(OCH_3OH)_6(CH_3OH)_{10}Cl_2$. Other
magnesium diaryloxides such as magnesium di-
isopropoxide, magnesium diethoxide, magnesium
dibutoxide, magnesium diphenoxide, magnesium
dinaphthoxide and ethyoxymagnesium isobutoxide.
Magnesium compounds as disclosed in U.S.
4,710,482 are preferred, especially
$Mg_4(OCH_3)_6(CH_3OH)_{10}X_2$ wherein X is a resorcinol or
substituted resorcinol monoanion. Also useful
are magnesium compounds which have one alkyl or
aryl group and one alkoxy or aryloxy group.
Examples of these compounds are phenylmagnesium
phenoxide, ethylmagnesium butoxide,
ethylmagnesium phenoxide and naphthylmagnesium
isoamyloxide.

The reaction of the magnesium oxy compound
and the tetravalent titanium halide,
conventionally termed a halogenation reaction,
produces a magnesium halide in which the atomic
ratio of halogen to magnesium is at least 1.2.
Preferred reaction products are those in which
the halogenation proceeds more completely, i.e.,
the reaction product has an atomic ratio of
halogen to magnesium of at least 1.5. Except in
those instances wherein the magnesium compound
contains a phenoxide moiety, e.g., a resorcinol
moiety, the most preferred reactions produce a
fully halogenated reaction product. The
halogenation reactions suitably employ a molar
ratio of magnesium compound to titanium compound
of from 0.005:1 to 2:1, preferably from 0.01:1
to 1:1. The halogenation reaction, as stated,
takes place in the additional presence of an

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electron donor and, optionally, a
halohydrocarbon diluent.

5   Suitable tetravalent titanium halides are
titanium tetrahalides or the corresponding
compounds of one or two alkoxy or aryloxy
substituents and three or two halide moieties,
respectively. Illustrative of these latter
titanium halides are dihexanoxytitanium
dichloride, diethoxytitanium dibromide,
10   isopropoxytitanium triiodide and phenoxytitanium
trichloride. the titanium tetrahalides are
particularly preferred, especially titanium
tetrachloride.

        The reaction of the magnesium compound and
15   the tetravalent titanium compound is conducted
in the presence of an electron donor. Suitable
electron donors include ethers, esters, ketones,
phenols, amines, amides, imines, nitriles,
phosphines, silanes, phosphites, stibines,
20   arsines, phosphoramides and alcoholates.
Examples of suitable electron donors are those
disclosed in U.S. 4,442,276. The preferred
electron donors are esters of aliphatic and
aromatic carboxylic acids, particularly acids of
25   two carboxyl groups. Illustrative esters
include dimethyl carbonate, dimethyl adipate,
dimethy, fumarate, dibutyl maleate,
ethylisopropyl oxalate, diethyl phthalate and
diisobutyl phthalate. The most preferred
30   electron donors of the halogenation reaction are
dialkyl phthalates.

        Suitable halohydrocarbons useful as the
optional component of the halogenation reaction
include aliphatic halides and aromatic halides.
35   Aliphatic monohalides such as butyl chloride and

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amyl chloride are suitable but preferred
aliphatic halides have from 1 to 12 carbon atoms
per molecule, preferably from 1 to 9 carbon
atoms per molecule, and at least two halogen
5   atoms. Illustrative of such preferred aliphatic
halohydrocarbons are dibromomethane,
trichloromethane, 1,2-dichloroethane,
dichlorobutane, 1,1,1-trichloroethane,
trichlorocyclohexane, dichlorofluoroethane,
10   trichloropropane, trichlorofluorooctane,
dibromodifluorodecane, hexachloroethane, carbon
tetrachloride and tetrachloroisooctane. The
preferred aliphatic halohydrocarbons are carbon
tetrachloride and 1,1,1-trichloroethane.
15   Suitable aromatic halohydrocarbons include
chlorobenzene, bromobenzene, dichlorobenzene,
dichlorodibromobenzene, chloronaphthalene,
chlorotoluene and dichlorotoluene. The
preferred aromatic halohydrocarbons are
20   chlorobenzene and dichlorobenzene, especially
chlorobenzene.
         The halogenation typically results in the
production of a solid reaction product which, in
one embodiment, is isolated from the product
25   mixture by filtration, decantation or other
conventional procedure. The product is suitably
washed with inert hydrocarbon as described below
to remove any unreacted, absorbed material. In
a preferred embodiment, however, the initial
30   reaction product is contacted with additional
tetravalent titanium halide which is the same or
is a different tetravalent titanium halide from
that previously used. For this contacting also,
the preferred tetravalent titanium halide is a
35   titanium tetrahalide, particularly titanium

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tetrachloride. This contacting serves to
increase the halide content of the solid
catalyst component. The halide content is
preferably greater than 90% of the ionic
5   equivalents of magnesium plus titanium in the
solid catalyst component. This contacting is
suitably conducted at a temperature of from 60°C
to 136°C over a period of 0.1 hour to 6 hours in
the option presence of an inert hydrocarbon
10   diluent. The contacting, conducted with one or
with several portions of tetravalent titanium
halide, is preferably effected at a temperature
of from 70°C to 120°C with a contact time of
about 0.5 hour to about 3.5 hours. After the
15   treatment with tetravalent titanium halide, the
solid catalyst component, i.e., the procatalyst,
is isolated from the media of its production by
conventional methods and washed to remove
unreacted titanium compounds. the titanium
20   content of the final, washed, catalyst component
is suitably up to about 4.5% by weight and
preferably from 1.5 to 3.6% by weight. The
product contains magnesium and titanium species,
preferably present as predominantly the
25   chlorides.
        The material employed to wash to solid
catalyst component is an inert, light
hydrocarbon diluent. The hydrocarbon is
aliphatic, alicyclic or aromatic but is
30   preferably an aliphatic hydrocarbon such as
isopentane, n-hexane and isooctane. Isopentane
is particularly preferred. The quantity of
light hydrocarbon to be used is from 5 cc to 100
per gram of procatalyst in each of from 2 to 6
35   separate washes and preferably about 25 cc

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hydrocarbon per gram of procatalyst in each
wash. The resulting solid product is the
procatalyst from which, together with the
organoaluminum compound (cocatalyst) and

5   selectivity control agent, the polymerization
catalyst is formed.

The organoaluminum compound cocatalyst is
usefully any of the known aluminum-containing
activators in olefin polymerization catalysts

10   which are based on a titanium halide including
dialkylaluminum halides or alkylaluminum
dihalides. Preferably, however, the
organoaluminum compound is halide free and best
results are obtained if at least the major

15   proportion off the organoaluminum compound is a
trialkylaluminum wherein each of the alkyl
groups has 1 to 6 carbon atoms.
Trimethylaluminum, triethylaluminum, tri-n-
propylaluminum, tri-i-propylaluminum, tri-i-

20   butylaluminum and dibutylamylaluminum are
illustrative. The trialkylaluminum is, on
occasion used in combination with an
alkylaluminum halide, e.g., diethylaluminum
chloride, but preferably the sole organoaluminum

25   compound is a trialkylaluminum.

The organoaluminum compound is used in
combination with a selectivity control agent
which is provided separately or in combination
(complex) with the organoaluminum compound. The

30   selectivity control agent is employed in an
amount of from 1 mol to 100 mols per mol of
titanium compound of the procatalyst, preferably
from 10 mols to 80 mols per mol of titanium
compound. In the present invention, the

35   selectivity control agent is an aromatic

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heterocyclic nitrogen compound, the choice of
which will largely determine the degree of
elasticity and the stereoregular character of
the polyolefin product produced in the process
5   which utilizes the olefin polymerization
catalyst.

The aromatic heterocyclic nitrogen
compounds which are employed in the process of
the invention are those where at least one
10   nitrogen is not unduly hindered by the presence
of substituent groups on adjacent carbon atoms,
e.g., the nitrogen is unhindered by the presence
of substituent groups or adjacent carbon atoms
or is "effectively" hindered by such groups. By
15   the term "effective" hindrance is meant steric
hindrance by substituent groups located on
adjacent carbon atoms which are not so bulky as
to prevent the formation of an elastomeric,
primarily stereoregular polyolefin. Without
20   wishing to be bound by any particular theory, it
is considered likely that if the substituent
groups are too bulky, the aromatic heterocyclic
nitrogen compound will not be able to coordinate
with other components of the catalyst system and
25   will not provide stereochemical control.

In one embodiment of the invention the
selectivity control agent is an unhindered.
aromatic heterocyclic nitrogen compound and the
catalyst prepared therewith serves to produce
30   elastomeric, primarily isotactic polymers
according to the process of the invention. The
aromatic heterocyclic nitrogen compound is
effectively unhindered when at least one
heterocyclic nitrogen atom is substituted on at
35   least one adjacent carbon atom with a hydrogen.

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Thus, the use of pyridine as a selectivity
control agents produces the elastomeric,
primarily isotactic polypropylene as does a
substituted pyridine substituted by other than
5   hydrogen on one adjacent carbon atom, e.g.,
acridine. Alternatively, use of an acridine
containing a methyl group substituent on the
available carbon atom adjacent to the nitrogen
does not result in the production of primarily
10 isotactic polymer. The presence of a bulky
substituent on each adjacent carbon atom, e.g.,
2,6-di-t-butylpyridine, does not result in
production of primarily stereoregular product.
Other unhindered aromatic heterocyclic nitrogen
15 compounds are pyrazine, 3,4,5-trichloropyrazine,
1,3,5-triazine, phenazine, 2,6-dimethylpyrazine,
quinazoline, 2-picoline, quinoline, 2-
methylpyrazine and 2,4-dichloropyrimidine.
In a second embodiment of the invention,
20 the selectivity control agent is a less
effectively hindered aromatic heterocyclic
nitrogen compound wherein at least one of the
substituents on the adjacent carbon atoms of
each nitrogen provide some degree of hindrance
25 but such hindrance is insufficient to prevent
the production of elastomeric, primarily
isotactic polymer. Such substituents are
methoxy, chloro or a portion of a fused aromatic
ring. Illustrative of such aromatic
30 heterocyclic nitrogen compounds are 2,6-
dichloropyridine, 2-chloroquinoline, 2-chloro-6-
methoxypyridine and 2,4,5,6-
tetrachloropyrimidine.
In the third embodiment of the invention
35 the selectivity control agent is an effectively

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hindered aromatic heterocyclic nitrogen compound
wherein the steric hindrance arises from the
presence of substituents on the carbon atoms
adjacent to each nitrogen atom are hindered by
groups other than chloro or methoxy or a fused
aromatic ring. Use of a catalyst formed from,
inter alia, such a selectivity control agent
results in the formation of an elastomeric,
primarily stereoregular polymer which in this
embodiment is a syndiotactic polymer.
Illustrative of this class of aromatic
heterocyclic nitrogen compounds are 2,6-
lutidine, 2,4,6-collidine, 2,3-
dimethylquinoxaline and tetramethylpyrazine.

        To prepare the final polymerization
catalyst, the procatalyst, cocatalyst and the
selectivity control agent are simply combined,
preferably employing the components in
quantities sufficient to provide in the catalyst
an atomic ratio of aluminum to titanium of from
1 to 150, particularly from about 10 to about
150, although higher ratios may be used. In
general, an increase in the ratio of aluminum to
titanium results in greater catalyst activity
but leads to increased catalyst residues in the
unextracted product. The atomic ratio will vary
depending upon the process and product desired.
Atomic ratios of aluminum to titanium from 30 to
100 are most advantageous, particularly ratios
from 50 to 80.

        Polymerization of the α-olefins such as
propylene according to the invention is
conducted in a liquid system with a diluent such
as a paraffinic liquid of 3 to 15 carbon atoms
per molecule or in a liquid system containing

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propylene as the dilent employed alone or in
combination with a small amount of propane.
Liquid-phase propylene polymerization is
conducted at a temperature of 50°C to 80°C and a
5   pressure sufficient to maintain liquid
conditions. The process is suitably conducted
batchwise but preferably is effected by a
continuous reaction. In the latter system the
liquid in the reaction zone is maintained at
10   reaction conditions, monomer is continuously
charged to the reaction zone, catalyst
components are also charged continuously or at
frequent intervals and reaction mixture
containing polymer is withdrawn from the
15   reaction zone continuously or at frequent
intervals. Under these conditions, the polymer
is produced as a slurry in the reaction mixture
and is recovered by conventional methods and the
reaction mixture is suitable for recycle. The
20   catalyst of the invention is sufficiently active
and specific in propylene polymerization so that
removal of catalyst residues or atactic polymer
from the polypropylene product is not required.
The process and catalyst are particularly suited
25   for operation in a continuous liquid phase
reaction but alternatively are useful in a
batchwise liquid phase process or in a vapor
phase reaction.
       It is well known that supported
30   coordination procatalysts and catalyst systems
of the type used in the present process are
highly sensitive, in varying degrees, to
catalyst poisons such as moisture, oxygen,
oxides of carbon, polyolefins, acetylenic
35   compounds and sulfur compounds. It should be

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understood that in the practice of the invention
both the physical equipment and the reactants
and diluents are carefully dried and free of
catalyst poisons.

5   The polymer products according to the
process of the invention are elastomeric,
primarily stereoregular poly-α-olefins derived
from olefins of at least 3 carbon atoms. The
polymers are characterized by the presence of a

10   narrow distribution of relatively short block
lengths and relatively high tensile strength.
They are distinguished from other polyolefins by
the combination of elastomeric properties and
strength.

15   The invention is further illustrated by the
following Examples which should not be regarded
as limiting. In the examples, the productivity
of the procatalyst is determined as kg polymer/g
procatalyst in a standard one hour batch

20   reaction. Catalyst activity is sometimes
reported as kg polymer/g procatalyst hr or kg
polymer/g Ti hr. The specificity towards the
production of stereoregular polymers, either
syndiotactic or isotactic, is determined by

25   measurements involving the pentads observed in
the ^{13}C-NMR spectrum. See Randall, "Polymer
Sequence Determination, Carbon-13 NMR Method,"
Academic Press, N.Y., 1977. A relationship has
been determined to estimate the average block

30   length by measuring the amount of xylene soluble
polymer (SX) in accordance with regulations of
the U.S. Food and Drug Administration. A XS
test is conducted by dissolving a polymer sample
is xylene in a stirred flask at 120°C. The flask

35   is then immersed in a water bath at 25°C without

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stirring for 1 hour, during which the insoluble
portion precipitates. The precipitate is
removed by filtration and the solubles present
in the filtrate are determined by evaporating a

5   20 ml aliquot of the filtrate, drying the
residue under vacuum and weighing the residue.
The xylene soluble content increases for short
block length material and may include some
amorphous or low molecular weight crystalline

10   material. See FDA regulations 121.2501 and
121.2510, 1970. The desirable numerical value
for polypropylene polymers produced according to
the invention is between about 35% and about
85%.

15   <u>Preparation of Procatalysts</u>
<u>Procatalyst A:</u> Magnesium methoxide solution
(12%) was prepared by dissolving magnesium metal
in methanol containing 0.125 equivalent of
tetraethoxysilane (TEOS) and then filtering

20   through a medium porosity fritted glass filter
to remove the slight amount of grey suspension.
        The magnesium methoxide solution (791 g,
1.10 mol) was added slowly, at 60°C, to a
solution of resorcinol (60.5 g, 0.55 mol) in

25   methanol (175 g) while stirring at 450 rpm with
a 3-inch wide, curved teflon paddle of 1.5 in^2
surface area. By the time one-third of the
methoxide had been added the flocculant
precipitate had gotten quite viscous so another

30   155 g of methanol was added. After addition was
complete the reaction was stirred for an hour
then filtered. The solids were washed with
methanol then isooctane then dried under moving
nitrogen to yield crystalline cylindrical rods

35   of formula: $Mg_4(OCH_3)_6(CH_3OH)_{10}(resorcinolate)_2$.

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Partial desolvation of this precursor was
carried out by boiling 40 g of solids in 300 g
of cyclohexane, containing 120 g of
tetraethoxysilane, until the volume had
5   decreased by 20-30%.
         The procatalyst was prepared by stirring
7.8 g of the partially desolvated precursor in
200 ml of a 50/50 (vol/vol) mixture of
$TiCl_4$/chlorobenzene. After adding
10   isobutylphthalate (2.5 ml, 8.7 mmol) the mixture
was heated in an oil bath and stirred at 115°C
for 60 minutes. The mixture was filtered hot
and the solids slurried in 200 ml of fresh
$TiCl_4$/chlorobenzene mixture. Phthaloyl chloride
15   (0.5 ml, 3.4 mmol) and p-toluoyl chloride (0.5
ml, 3.7 mmol) were added and the mixture stirred
at 115°C. After 60 minutes the mixture was
filtered hot and the solids slurried again into
200 ml of fresh $TiCl_4$/chlorobenzene mixture,
20   heated at 115°C for 30 minutes and filtered hot.
The solids were then slurried into 200 ml of
fresh $TiCl_4$/
chlorobenzene mixture, heated at 115°C for 30
minutes and filtered hot. The solids were then
25   slurried into 100 ml of fresh $TiCl_4$/chlorobenzene
mixture, heated at 115°C for 10 minutes and
filtered hot. The solids were allowed to cool
then washed with six 150 ml portions of
isopentane and dried for 100 minutes under
30   moving nitrogen at 40°C. Ti=2.54%.
         <u>Procatalyst B:</u> Magnesium ethoxide (8.2 g, 72
mmol) was slurried in 200 ml of 50/50 (vol/vol)
$TiCl_4$/chlorobenzene and then isobutyl phthalate
(2.5 ml, 8.5 mmol) was added at room
35   temperature. The gently stirring mixture was

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heated to 110°C and held for 1 hour. The mixture
was filtered hot and then another 200 ml of the
$TiCl_4$/chlorobenzene mixture was added along with
phthaloyl chloride (0.42 ml, 2.9 mmol) and ethyl

5   benzoate (0.37 ml, 2.6 mmol) and the gently
stirring slurry was held at 110°C for another 1.0
hour and filtered hot. The solids were slurried
in one final 200 ml portion of the
$TiCl_4$/chlorobenzene solvent mix and stirred

10   gently for 0.5 hour at 110°C. The mixture was
filtered hot and then allowed to cool to 40°C
before washing with six 150 ml aliquots of
isopentane. The resulting powder was dried for
100 minutes under moving nitrogen at 40°C. The

15   yield is 9 gm of procatalyst. Ti=2.70%.
Procatalyst C: Magnesium (104 g, 4.28 mol) was
added portionwise to a mixture of 1.2 liters of
methanol and 130 ml TEOS in a 3-liter-3-neck
flask. Overnight stirring yielded a

20   crystalline slush from which no solvent could be
decanted. 1500 ml of TEOS was added as the
slush was gently broken up with a spatula to
produce a thick milky slurry which turned cold
while stirring and turned white and thickened

25   over an hour of stirring. The extremely thick
slurry was diluted in two steps: 66% was
diluted with 700 ml TEOS and 33% of that was
diluted to 21 with TEOS to provide a milky
slurry containing the equivalent of 22 g

30   magnesium.
        This slurry was heated gradually to a pot
temperature of 153°C as distillate was collected
over a 2 hour period. Microscopic examination
revelated glassy granular particles in a narrow

35   size distribution around 15 micron.

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The granular particles (8.2 g, 56 mmol) were slurried in 200 ml of a 50/50 (vol/vol) mixture of $TiCl_4$/chlorobenzene. After adding isobutylphthalate (2.5 ml, 8.7 mmol) the mixture was heated in an oil bath and stirred at 110°C for 60 minutes. The mixture was filtered hot and the solids slurried in 200 ml of fresh $TiCl_4$/chlorobenzene mixture. Phthaloyl chloride (0.42 ml, 2.9 mmol) and ethyl benzoate (0.37 ml, 2.6 mmol) were added and the mixture stirred at 110°C. After 60 minutes the mixture was filtered hot and the solids slurried again into 200 ml of fresh $TiCl_4$/chlorobenzene mixture. The slurry was stirred for 30 minutes at 110°C then filtered hot. The solids were allowed to cool to 40°C and then washed with six 150 ml portions of isopentane and dried for 100 minutes under moving nitrogen at 40°C. The yield was 8.0 g of pink procatalyst. Analysis: 2.55% Ti.

Procatalyst D: Prepared from 330 lb of $Mg(OEt)_2$ using the same procedure and molar ratios as described for procatalyst B. Ti=2.77%.

Examples 1-5

Procatalysts were used as a 5% slurry in mineral oil. Triethylaluminum (TEA) was used as a 0.28 M solution in isooctane, diethylaluminumchloride (DEAC) was used as a 1.54 M solution in heptane and tetramethylpyrazine was used as a 12% solution in isooctane. Examples 1-4 illustrate the effect of using tetramethylpyrazine as selectivity control agent (SCA) with four procatalysts (A-D above). Example 5 is a comparative example in which the tetramethylpyrazine had been omitted.

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Triethylaluminum (1.2 mmol) and
tetramethylpyrazine (0.24 mmol) were mixed
together and then an amount of procatalyst
slurry containing 0.012 mmol Ti was mixed with
5   that. After 20 minutes, 0.60 ml of DEAC was
added to produce the total catalyst mixture.
TEA (1.4 mmol) was then injected to 2.7 liters
of propylene in a rapidly stirring 1 gallon
stainless steel autoclave at 65°C followed by the
10   total catalyst mixture and polymerization was
carried out for about 200 minutes at 65°C. After
evaporation of excess propylene and cooling to
room temperature the polymers were removed as a
lump from the reactor then cut into pieces and
15   allowed to dry overnight in a fume hood prior to
characterization.

The productivities, the xylene solubles
content and the bulk polymer composition (as
determined by NMR spectroscopy) for rubbery
20   polymers of Examples 1-4 are listed in Table 1.
This polymer is primarily isotactic.

The pertinent properties for the polymers
are shown in Table 2. Note that the tensile set
values indicate that the primarily syndiotactic
25   polymers of Examples 1, 3 and 4 are highly
elastic (Tset, after stretching to 300% length,
of only 22-28%) whereas the primarily isotactic
control case of example 5 is not as elastic
(Tset of 120%).

TABLE 1

Productivity and Composition of the Bulk Polypropylene From Various Phthalate Based Catalysts

Example	Catalyst No.	Xylene Sol. (% wt)	Productivity (Kg PP/g cat hr)	Syndiotactic (mol %)	Lsyn (ave)	Isotactic (mol %)	Liso (ave)	Defective (mol %)
1	A	79.0	8.5	51	7	24	9	26
2	B	63.8	4.8	52	7	22	8	26
3	C	80.8	7.1	49	6	25	9	26
4	D	56.6	8.4	49	7	26	10	25
5	*	41.7	3.5	20	7	64	19	16

*Control, no SCA was used.

TABLE 2

Properties of the Polymers from the Various Catalysts Examined

Example	Catalyst No.	Melt Flow (dg/min)	Tensile Set (20%)	Tensile Yield (psi)	Tensile Break (psi)	Elongation at Break (%)
1	A	2.08	28%	500	883	>917
3	C	1.67	22%	441	836	>1000
4	D	2.06	24%	499	875	>1000
5	*	0.39	120%	1764	2837	770

*Control, no SCA was used.

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Examples 6-16 (SCA's producing primarily syndiotactic polymer)

The only cocatalyst used was
triethylaluminum as a 0.28 molar solution in
isooctane. A 0.20 mmol sample of the
selectivity control agent, 0.01 mmol of the
procatalyst and 0.7 mmol of the cocatalyst were
mixed together and after 20 minutes were
injected into 2700 ml of liquid propylene in a
reactor where the polymerizations were carried
out for 90 minutes at 60°C. Procatalyst A was
used throughout.

^{13}C Magnetic Resonance

Spectra were obtained at 135°C on samples
dissolved in 1,2,4-trichlorobenzene. The
spectrum reference was the mmmm methyl group
assigned at 21.68 ppm. The calculated results
of % syndiotactic, % isotactic, % defective and
the respective average block lengths, for the
boiling isooctane fractionated polymer are shown
in Tables 3 and 4.

Tensile Properties

In order to prepare samples for tensile
measurements, about 60 g of the polymer was
blended in a Brabender mixer at 190°C with 0.3 g
of IRGANOX®1010 antioxidant. After cooling, a
6" x 6" x 2mm plate was compression molded at
204°C under 5 tons pressure. Tensile bars were
then cut from the plate using a 'C' die. The
measurement conditions are as described in ASTM
D 412-83. Tensile set is the residual
elongation imparted to a sample after stretching
to an increase of 300% over its original length
at a rate of 20 inches/minute and then allowing
it to recover to zero load at that same rate.

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Tensile yield is the stress required to induce a
permanent deformation in the sample. Tensile at
break is the stress required to break the sample
at an elongation rate of 20 inches/minute.
Elongation at break is the measured elongation
at the break condition.

Melt flow index was determined under
condition L (2160 g, 230°C) on a Tinius Olsen
Plastometer. The strands, which were formed by
extrusion through the 3mm die of the melt flow
device, were stretched to an equilibrated length
by hand pulling to nearly the break point
several times. The diameter of the stretched
strand is reported as the average of several
measurements along the length of the strand.
The elasticity of the polymer is reported as the
percentage elongation obtained upon applying a
force nearly enough to break the strand (after
which, of course, the strand returns to its
equilibrated length). This measurement is
essentially equivalent to the reversible elastic
elongation described by G. Natta et al in U.S.
3,175,999.

Table 5 shows the tensile properties for
certain of the polymers produced.

TABLE 3
(Less Hindered Heterocycles)

Example	SCA	% Syn	Lsyn	% iso	Liso	Lave	X.S. (%)	Stretch
5	None	22	6.7	60	14	12.0	42.4	20%
6	2-picoline	19	6.3	62	14	12.2	49.4	9%
7	Quinoline	21	6.7	61	15	12.9	44.4	14%
8	2,3,5-trimethyl pyrazine	12	6.9	77	25	22.6	23.1	10%
9	Phenazine	21	7.0	62.5	17	14.5	36.4	14%
10	Acridine	18	6.8	64	17	14.8	31.0	21%

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TABLE 4
(Hindered Heterocycles)

	Example	SCA	% Syn	Lsyn	% iso	Liso	Lave	X.S. (%)	Stretch
5	11	2,6-Lutidine	54.5	8.7	25	10	9.1	67.6	68%
	12	Quinaldine	52	8.9	27	12	10.0	62.4	110%
	13	2,3,5,6-Tetra-methylpyrazine	50	7.7	25	9	8.1	79.1	80%
	14	2,4,6-Collidine	49	8.8	30	10	9.3	69.1	113%
10	15	2,3-Dimethyl-quinoxaline	45	8.0	34	13	10.2	61.4	58%
	16	2,4-Dimethyl-quinoline	42	8.4	37	13	10.6	61.3	78%

TABLE 5
Tensile Properties

	Example		Tset*	Tyield (psi)	Tbreak (psi)	Elongation @ break %
	6	Iso	171%	1289	2402	843
	10	Iso	204%	1529	2893	785
20	11	Syndio	65%	730	1554	750
	12	Syndio Compar	73%	822	1845	769
	13	Syndio Compar	52%	587	1114	908
	14	Syndio	110%	980	1651	764

*Stretch to 400% of original length.

Examples 17-19

Using two different relatively less
hindered heterocyclic selectivity control agent,
which are the subject of this invention, and one
effectively hindered heterocycle, 1.8 liters of
1-butene was polymerized under the same
conditions used above for propylene
polymerizations. The NMR results presented in
Table 6 show that the less hindered SCAs
(Example 14 and Example 15) produce
predominantly isotactic polybutylene while the
methyl hindered SCA (Example 16) produced
primarily syndiotactactic polybutylene. The

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tensile properties of these examples are shown
in Table 7. As with the polypropylene case the
polybutenes of the present invention exhibit
higher tensile strength and higher tensile set
5   values than the polymer of the more hindered
nitrogen heterocycle (i.e., they are only mildly
elastomeric).

TABLE 6
Polybutylene

Example	SCA	% Iso	<Liso>	% Syn	<Lsyn>
17	2,3,5-trimethylpyrazine	51	12	19	5.9
18	Cyanuric chloride	68	18	12	5.6
19	2,6-lutidine	27	10	38	6.9

TABLE 7
Polybutene Tensiles

Example	Tensile set	Tensile at break	Elongation at break
17	100%	974 psi	590%
18	158%	2852 psi	480%
19	30%	>230 psi*	>1000%

20   *Sample did not break at 1000% elongation.

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WHAT IS CLAIMED IS:

1.   A process for the production of elastomeric, primarily stereoregular poly-α-olefin, wherein the α-olefin is of at least 3 carbon atoms, characterized by short average block lengths which comprises polymerizing the α-olefin in the presence of a catalyst which comprises:

a)   the reaction product of a magnesium oxy compound and a tetravalent titanium compound wherein the reaction takes place in the presence of an electron donor;

b) an organoaluminum compound; and

c) a selectivity control agent which is an aromatic heterocyclic nitrogen compound which is not unduly hindered by the presence of substituents on carbon atoms adjacent to at least one nitrogen atom.

2.   The process of claim 1 for the production of elastomeric, primarily syndiotactic polypropylene wherein each nitrogen of the aromatic heterocyclic nitrogen compound is effectively hindered.

3.   The process of claim 2, wherein the nitrogen compound is selected from 2,3-dimethylquinoxaline, quinaldine, 2,6-lutadine, 2,4,6-collidine or tetramethylpyrazine.

4.   The process of claim 3, wherein the tetravalent titanium halide is titanium tetrachloride.

5.   The process of claim 4, wherein the magnesium compound is a compound of the formula MgR_1R_2 wherein R_1 is alkoxide or aryloxide and R_2 is alkyl, aryl, alkoxide, aryloxide or halogen.

6.   The process of claim 5, wherein R_1 and

R_2 are ethoxide.

7. The process of claim 5, wherein the magnesium compound is of the formula $Mg_4(OCH_3)_6(CH_3OH)_{10}X_2$ wherein X is a resorcinol or substituted resorcinol monoanion.

8. The process of claim 1 for the production of elastomeric, primarily isotactic poly-α-olefin wherein each nitrogen of the aromatic heterocyclic nitrogen compound is less hindered by the presence of chloro or methoxy groups on at least one adjacent carbon atom.

9. The process of claim 8, wherein the nitrogen compound is 2,6-dichloropyridine, 2-chloroquinoline, 2-chloro-6-methoxypyridine, 2,3-dichloroquinoxaline, 2,4,6-trichloropyrimidine or 2,4,5,6-tetrachloropyrimidine.

10. The process of claim 9, wherein the tetravalent titanium halide is titanium chloride.

11. The process of claim 10, wherein the magnesium compound is of the formula MgR_1R_2 wherein R_1 is alkoxy or aryloxy and R_2 is alkoxy, aryloxy or halogen.

12. The process of claim 11, wherein R_1 and R_2 are ethoxide.

13. The process of claim 11, wherein the magnesium compound is of the formula $Mg_4(OCH_3)_6(CH_3OH)_{10}X_2$ wherein X is a resorcinol or substituted resorcinol monoanion.

14. The process of claim 8, wherein the α-olefin is propylene.

15. The process of claim 8, wherein the α-olefin is 1-butene.

16. The process of claim 1 for the

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production of elastomeric, primarily isotactic poly-α-olefin wherein at least one nitrogen of the aromatic heterocyclic nitrogen is unhindered.

5　　　　17.　The process of claim 16 wherein the nitrogen compound is pyrazine, 3,4,5-trichloropyridazine, 1,3,5-triazine, phenazine, pyridine, 2,6-dimethylpyrazine, quinazoline, 4,6-dichloropyrimidine, 2-picoline, 2,3,5-

10　　trimethylpyrazine, acridine, 2-methylpyrazine, 2,5-dimethylpyrazine, 2,3-dimethylpyrazine, 2,3-dichloroquinoxaline, quinoline, pyridazine or 2,4-dichloropyrimidine.

　　　　18.　The process of claim 17, wherein the

15　　tetravalent titanium halide is titanium tetrachloride.

　　　　19.　The process of claim 18, wherein the magnesium compound is of the formula MgR_1R_2 wherein R_1 is alkoxide or aryloxide and R_2 is

20　　alkoxide, aryloxide or halogen.

　　　　20.　The process of claim 19, wherein R_1 and R_2 are ethoxide.

　　　　21.　The process of claim 19, wherein the magnesium compound is of the formula

25　　$Mg_4(OCH_3)_6(CH_3OH)_{10}X_2$ wherein X is a resorcinol or substituted resorcinol monoanion.

　　　　22.　The process of claim 16, wherein the α-olefin is propylene.

　　　　23.　The process of claim 16, wherein the

30　　α-olefin is 1-butene.

　　　　24.　A catalyst for use in the production of elastomeric, primarily stereoregular poly-α-olefin, wherein the α-olefin has at least 3 carbon atoms, characterized by short average

35　　block lengths which comprises:

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a) the reaction product of a magnesium oxy compound and a tetravalent titanium halide wherein the reaction takes place in the presence of an electron donor;

b) an organoaluminum compound; and

c) a selectivity control agent which is an aromatic heterocyclic nitrogen compound which is not unduly hindered by the presence of substituents on carbon atoms adjacent to at least one nitrogen atom.

25. The catalyst of claim 24, wherein the tetravalent titanium compound is titanium tetrachloride.

26. The catalyst of claim 25, wherein the magnesium oxy compound is of the formula MgR_1R_2 wherein R_1 is alkoxy or aryloxy and R_2 alkoxy, aryloxy or halogen.

27. The catalyst of claim 26, wherein the nitrogen compound is 2,3-dimethylquinoxaline, quinaldine, 2,6-lutadine, 2,4,6-collidine or 2,4-dimethylquinoline.

28. The catalyst of claim 27, wherein R_1 and R_2 are ethoxy.

29. The catalyst of claim 27, wherein the magnesium oxy compound is of the formula $Mg_4(OCH_3)_6(CH_3OH)_{10}X_2$ wherein X is a resorcinol or substituted resorcinol monoanion.

30. The catalyst of claim 26, wherein the nitrogen compound is 2,6-dichloropyridine, 2-chloroquinoline, 2-chloro-6-methoxypyridine, 2,3-dichloroquinoxaline, 2,4,6-trichloropyrimidine or 2,4,5,6-tetrachloropyrimidine.

31. The catalyst of claim 30, wherein R_1 and R_2 are ethoxy.

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32. The catalyst of claim 30, wherein the magnesium oxy compound is of the formula $Mg_4(OCH_3)_6(CH_3OH)_{10}X_2$ wherein X is a resorcinol or substituted resorcinol monoanion.

5   33. The catalyst of claim 26, wherein the nitrogen compound is pyrazine, 3,4,5-trichloropyridazine, phenazine, pyridine, 2,6-dimethylpyrazine, quinazoline, 2-methylpyrazine, 2,5-dimethylpyrazine, 1,3,5-triazine, 2,3,5-

10   trimethylpyrazine, acridine, 2,3-dimethylpyrazine, 2,3-dichloroquinoxaline, quinoline, pyridazine or 2,4-dichloropyrimidine.

34. The catalyst of claim 33, wherein R_1 and R_2 are ethoxy.

15   35. The catalyst of claim 33, wherein the magnesium oxy compound is of the formula $Mg_4(OCH_3)_6(CH_3OH)_{10}X_2$ wherein X is a resorcinol or substituted resorcinol monoanion.

INTERNATIONAL SEARCH REPORT

International Application No. **PCT/US90/02036**

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) 6

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5): C08F 4/654, 4/649, 10/06
U.S. CL. 526/124, 125, 141

II FIELDS SEARCHED

Minimum Documentation Searched 7

Classification System	Classification Symbols
U.S.	502/123; 526/124, 125, 141

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched 8

III. DOCUMENTS CONSIDERED TO BE RELEVANT 9

Category *	Citation of Document, 11 with indication, where appropriate, of the relevant passages 12	Relevant to Claim No. 13
Y	US, A, 4,754,006 (MURATA ET AL) 28 JUNE 1988 See column 9, line 67 to column 10, line 13.	1-8, 14-29, 33-35
Y	US, A, 4,107,413 (GIANNINI ET AL) 15 AUGUST 1978. See column 3, lines 25-31 and Example 11.	1-8, 14-29, 33-35
Y	US, A, 4,393,182 (GOODALL ET AL) 12 JULY 1983. See column 2, line 54-62.	1-8, 14-29,
Y	US, A, 4,710,482 (JOB) 01 DECEMBER 1987 See column 3, lines 9-14.	7, 21, 29, 35
Y	US, A, 3,534,006 (KAMAISHI ET AL) 13 OCTOBER 1970. See column 3, lines 46-67.	3-7, 17-21, 27-29,33-35
Y	US, A, 3,240,773 (BOOR) 15 MARCH 1966 See column 4, lines 3-14.	1-8, 14-29, 33-35

* Special categories of cited documents: 10

"A" document defining the general state of the art which is not considered to be of particular relevance

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
05 JULY 1990	0 9 AUG 1990
International Searching Authority	Signature of Authorized Officer
ISA/US	Edward J. Smith

Form PCT/ISA/210 (second sheet) (Rev.11-87)